CHEMISTRY IN HIGH TEMPERATURE PLASMA JETS

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INTRODUCTION

Plasma generators, in general, have been found suitable for a variety of uses. They generally provide an electric arc which is condensed or constricted into a smaller circular cross-section than would ordinarily exist in an open arc-type device. This constriction generates a very high temperature (8,000-20,000°K) so that a superheated-plasma working fluid can be ejected through the nozzle and the composition of the plasma determine the use to which the plasma generator is put. Plasma generators have been used for cutting, welding, metal spraying and chemical processing. For chemical processing, plasma generators have provided the possibility of the production of new alloys and compounds and the processing of less commonly used materials, as well as the preparation of certain common chemicals.

PLASMA JET EQUIPMENT

Two types of plasma generators are possible: the nontransferred and the transferred arc. A nontransferred arc consists of a cathode and a hollow anode where the arc is struck between the electrodes and the flame emerges through the orifice in the anode. In the transferred arc, the cathode is placed some distance away from the anode and an arc is passed between the electrodes. The nontransferred arc is the most popular in the chemical studies made to date.

A plasma jet used in chemical synthesis can have varied designs to meet special requirements, such as the introduction of a reactant material into the flame path at a particular point.

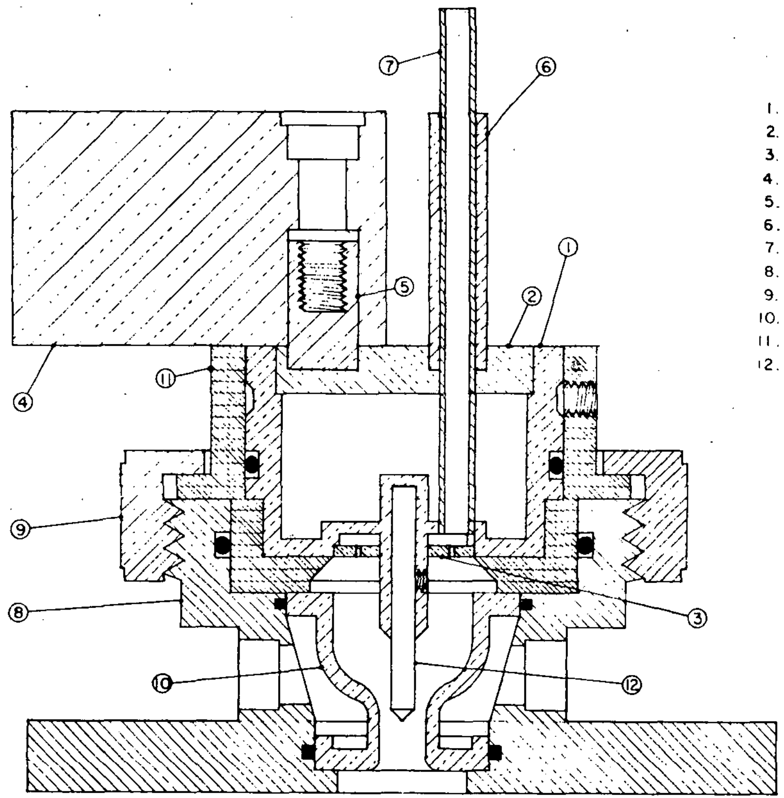
Consumable cathodes have been used in experiments in which carbon was one of the reactants. Carbon, vaporized from a graphite cathode, was used in the synthesis of cyanogen and hydrogen cyanide. Powdered carbon introduced in a gas stream or as a constituent of a gas has also been used as the source of carbon in a plasma flame.

Electrodes of 2%-thoriated tungsten are the most frequently used water-cooled nonconsumable electrodes. Water-cooled copper anodes have been widely used in experimen work. Figure 1 shows a typical plasma jet assembly. A reactor chamber may be of any configuration desired to accomodate different feeding and quenching devices.

PLASMA JET REACTIONS

GAS-GAS REACTIONS TO PRODUCE A GAS AND GAS DECOMPOSITION REACTIONS TO PRODUCE A GAS

A considerable amount of research has been done by a number of people in the area of plasma jet gas-gas reactions. The following is the gas reaction producing gases that have been investigated.



1. CATHODE ASSEMBLY
2. CATHODE TOP PLATE
3. GAS DISTRIBUTOR PLATE
4. CATHODE BUS BAR
5. CATHODE BUS BAR STUD
6. GAS ENTRY EXTENSION NIPPLE
7. GAS TUBE
8. ANODE ASSEMBLY
9. ANODE ASSEMBLY COVER
10. COPPER ANODE NOZZLE
11. NYLON INSULATOR
12. CATHODE

FIGURE 1

$$CH_4 \text{ (or other hydrocarbons) } \xrightarrow[\text{Ar Jet}]{H_2 \text{ Jet}} C_2H_2 \quad (1)$$

$$CH_4 + N_2 \xrightarrow[\text{Ar+N}_2 \text{ Jet}]{\text{Ar Jet}} HCN + C_2H_2 \quad (2)$$

$$CH_4 + NH_3 \xrightarrow[\text{Ar+N}_2 \text{ Jet}]{\text{Ar Jet}} HCN + C_2H_2 \quad (3)$$

$$CH_4 + H_2O \text{ (Gas)} \rightarrow CO + 3H_2 \quad (4)$$

$$N_2O_2 \xrightarrow{N_2 \text{ Jet}} NO \quad (5)$$

$$CF_4 + N_2 \rightarrow NF_3 + CF_3NF_2 \quad (6)$$

$$SF_6 + N_2 \rightarrow NF_3 \quad (7)$$

NH_3 or CH_4 cracking rate studies (8)

In the past several years considerable effort has been directed to the investigation of the production of acetylene from hydrocarbons (reaction 1).

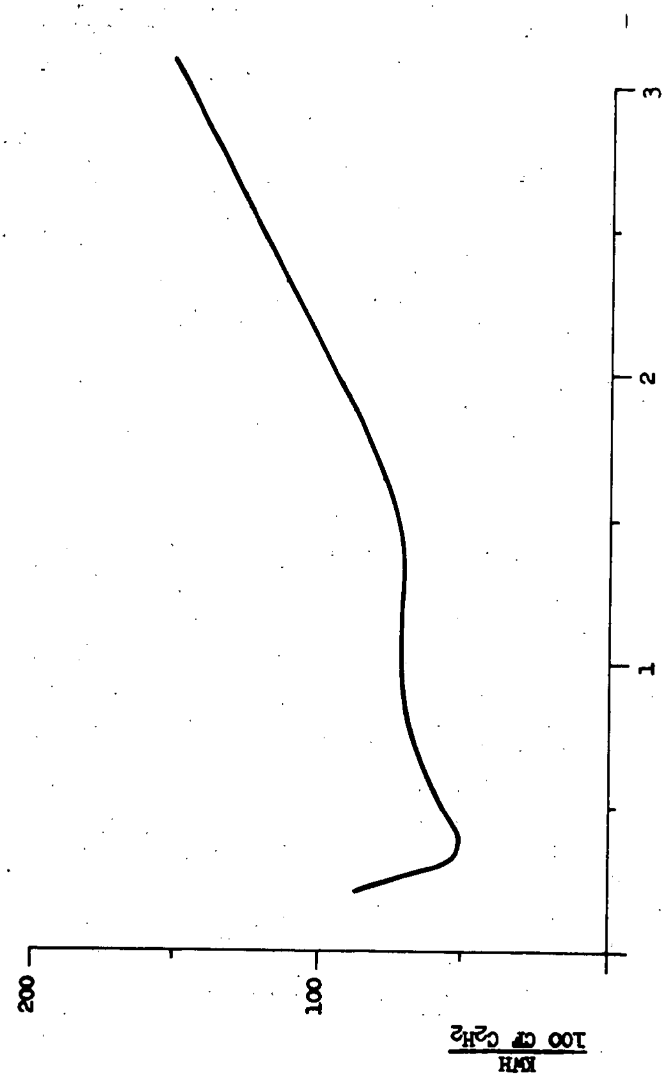
The production of acetylene by reacting methane in the flame of an argon plasma jet yielded an 80% conversion to acetylene [1]. Almost all of the methane was converted to acetylene and hydrogen with little formation of soot. Figure 2 shows the power consumption vs. the feed ratio of argon to methane. This ratio is the most important parameter in the acetylene yield. The minimum power consumption 60 Kwhr/100 cu. ft. acetylene produced, corresponded to a ratio of argon to acetylene of 0.3. Damon and White [2] selected the manufacture of acetylene as an application for plasma processing which might be of interest to the petroleum industry. Methane was one of the gases proposed with the use of recycle procedure. Anderson and Case [3] studied the methane decomposition reaction and compared it to available thermodynamic data. In these experiments a hydrogen plasma torch was used coupled to a reaction chamber and water quench system. The hot hydrogen stream emitted from the plasma jet, entered the reaction chamber and mixed with a methane feed. The gas mixture was analyzed after affluing from the reaction chamber and water quench system. The optimum cracking conditions for methane produced a 30% yield of acetylene.

In a report of the National Academy of Sciences [4] the investigation by the Linde Company of the production of acetylene using a plasma jet and natural gas was reported. This process is said to have a more efficient transfer energy to the feed stream than does the open arc process used in Germany.

Considerable research has been done on the methane-nitrogen and methane-ammonia reactions (reactions 2 & 3) to produce hydrogen cyanide and as a by product acetylene. Leutner [5 & 6] reported up to 50% conversions were obtained based on the carbon input (as methane) by using either nitrogen, argon or nitrogen-argon mixtures as the plasma gas. Figure 3 shows a schematic of the apparatus used in these studies. These experiments showed that up to 75% of the carbon input as methane was converted in HCN and acetylene for reaction 3 and 90% for reaction 2. No other hydrocarbons besides acetylene were found and cyanogen was present in only trace amounts.

Damon and White [7] proposed the production of reducer gas by reaction 4 using natural gas or propane as a hydrocarbon source. The proposed process=for steam-methane reforming would operate at a t emperature of 3000 to 6000°F and provide a high temperature reducing gas for metals and other high temperature processes.

The fixation of nitrogen (reaction 5) has been one of the major applications for arc induced reactions in the past. During the past several years direct fixation oxygen-nitrogen mixtures has been investigated, however, only 2% of the total nitrogen input has been converted to NO [6 & 8]. The use of liquid oxygen and/or liquid nitro



Feed Ratio Ar: CH_4

Figure 2

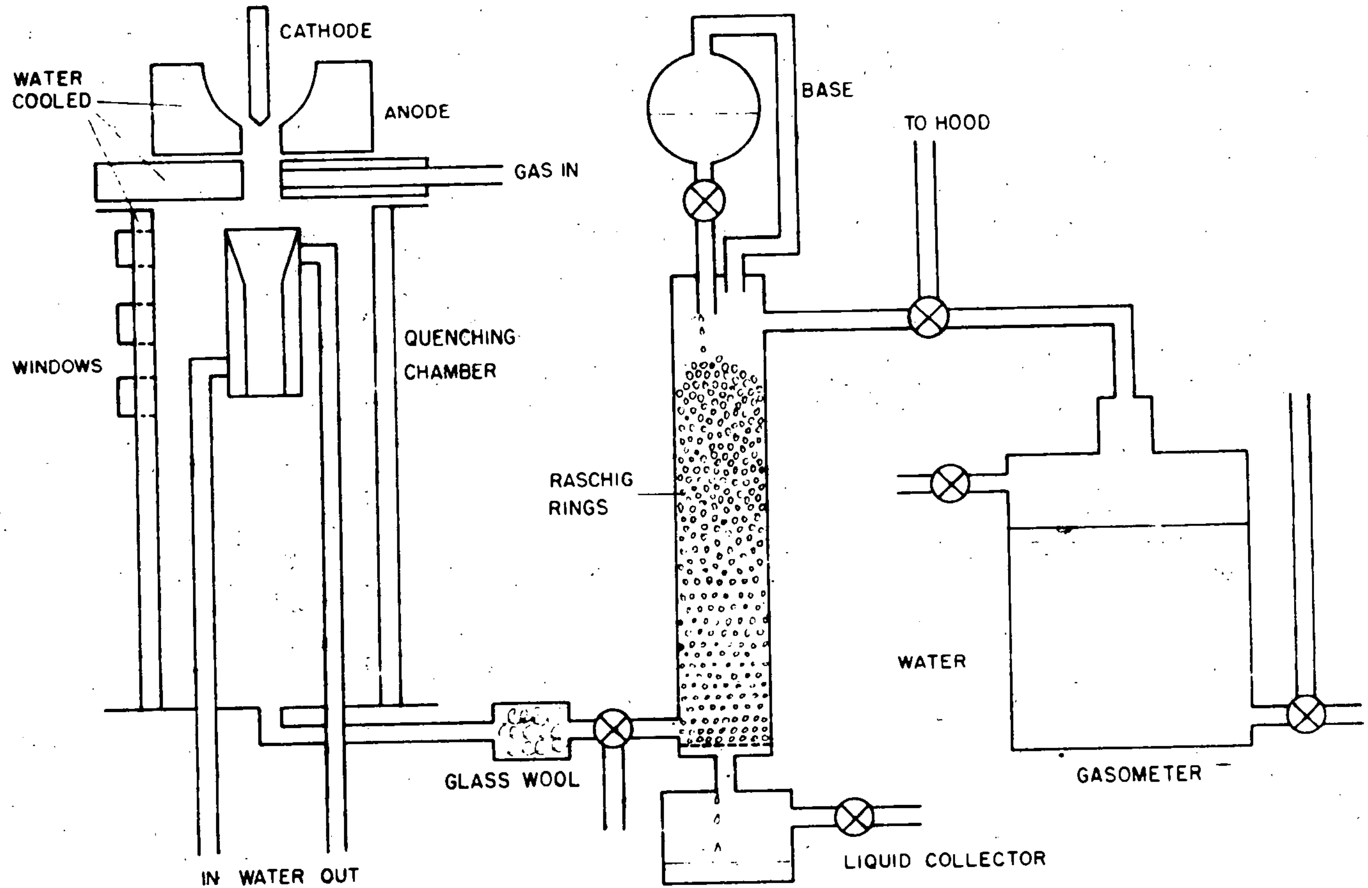

CATHODE
WATER
COOLED
ANODE
GAS IN
WINDOWS
QUENCHING
CHAMBER
IN WATER OUT
BASE
TO HOOD
RASCHIG
RINGS
GLASS WOOL
WATER
GASOMETER
LIQUID COLLECTOR

FIGURE 3

quench system with a nitrogen plasma jet have shown no improvement on the above yield(9).

Recently Bronfin and Hazlett [10] have experimented with the introduction of CF_4 and SF_6 into a nitrogen plasma jet. Small yields of NF_3, N_2F_4 and CF_3NF_3 (reactions of 6 & 7) were produced. The yield of fixed nitrogen compounds was of the order of 1% of the nitrogen inlet. The yield of these compounds increased with both increased power input and F/N ratio.

Freeman and Skrivan [11] have studied the decomposition rate of ammonia and methane in a plasma jet (reaction 8) and have shown it to be rate limited by a diffusion process. The apparatus used has been fully characterized and shown to be a very good fit for a diffusional model.

GAS-SOLID REACTIONS TO PRODUCE A-GAS

$H_2 + S \longrightarrow H_2S$ (1)

$C + H_2 \longrightarrow C_2H_2$ (2)

$C + H_2 + N_2 \longrightarrow HCN + C_2H_2$ (3)

$C + NH_3 \longrightarrow HCN + C_2H_2$ (4)

$C + N_2 \longrightarrow C_2N_2$ (5)

Recently investigations at the Research Institute of Temple University have shown that hydrogen sulfide can be synthesized from its element, hydrogen and sulfur powder fed in a helium plasma jet [12]. Conversions as high as 37% based on the sulfur input have been obtained. Figure 4 shows both the % conversion and the g/Kwhr of hydrogen sulfide formed vs. Kwhr/g of sulfur input. As can be seen from the figure the maximum conversion % does not necessarily have the maximum production efficiency.

A considerable number of synthesises have been carried out using solid carbon powder or graphite elements as a carbon source for reactions with various materials including hydrogen, nitrogen, hydrogen-nitrogen and ammonia. Reactions 2 through 5 show the various productions obtained by these reactions. In the case of acetylene synthesis (reaction 2) the highest yield obtained by direct synthesis from the elements was 33% [1]. Hydrogen cyanide yields up to 51% for reaction 3 and up to 39% for reaction 4 have been obtained [5]. A complete study of the synthesis of cyanogen from its elements was made by Leutner [6 & 13] and this reaction gave 15% conversion based on the carbon input at the optimum reaction conditions.

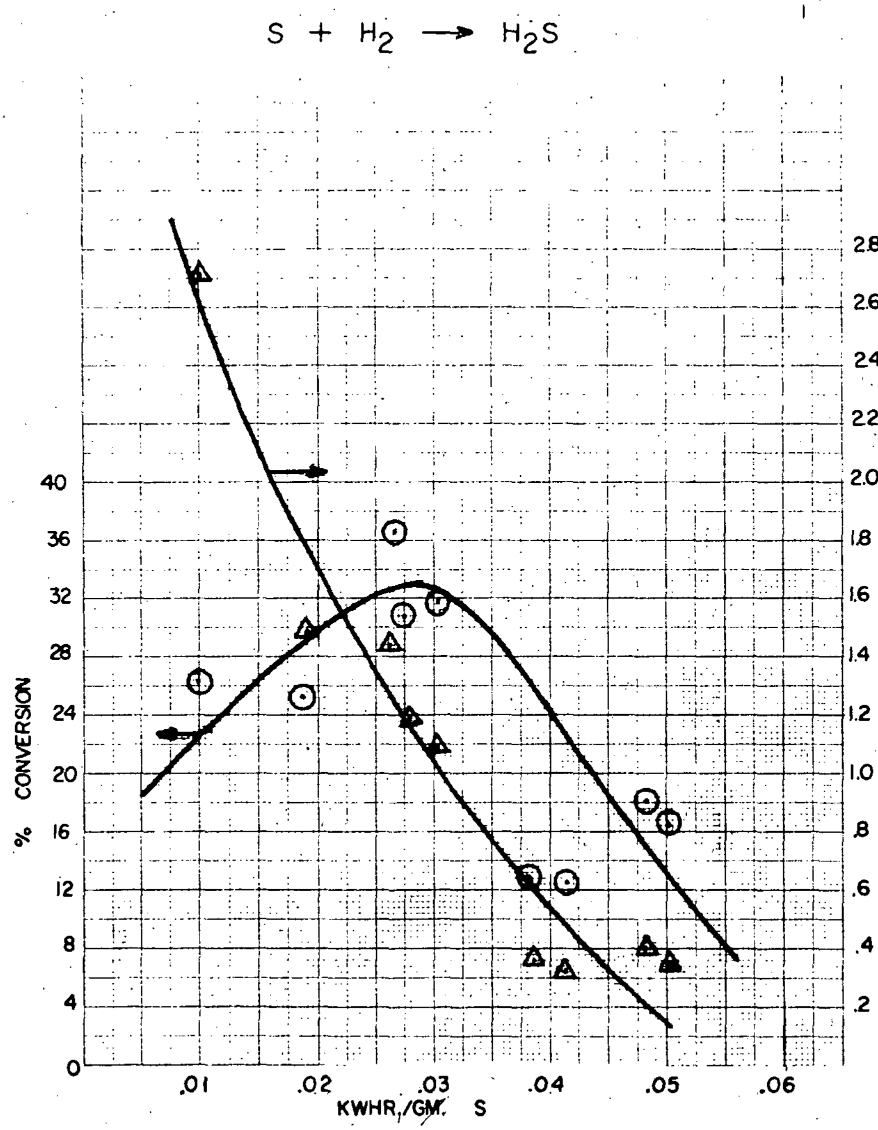
Recently Graves, Kawa and Hiteshue [14] reported investigations using bituminous coal fed into an argon plasma jet. Acetylene, the principal product, was obtained in yields of 15 wt. %. This work studied the effects of coal feed rate, particle size and plasma temperature on yields and products formed.

GAS-GAS REACTIONS TO PRODUCE A SOLID

$TiCl_4$ (gas) + NH_3 or N_2 + H_2 $\longrightarrow$ TiN (1)

Hydrocarbons $\longrightarrow$ C (2)

Harnisch, Kevmer and Schallus [15] reported the preparation of titanium nitride (reaction 1) from titanium tetrachloride gas with either plasma jet heated ammonia or nitrogen/hydrogen mixtures. The reaction produced very finely divided black titanium nitride up to 95% pure. The Thermodynamics Corporation [16] has



$S + H_2 \longrightarrow H_2S$
40
36
32
28
24
20
16
12
8
4
0
% CONVERSION
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
.8
.6
.4
.2
GM./KWHR. H_2S FORMED
.01
.02
.03
.04
.05
.06
KWHR./GM. S

FIGURE 4

reported the possibility of producing carbon black from hydrocarbons using a plasma jet. Methane or other hydrocarbons which would be introduced into the plasma flame, would be cracked using hydrogen as the operating gas and producing carbon black. Liquid as well as gaseous hydrocarbons can be used as a source for carbon and the Vitro Laboratories [4] have experimented with carbon black production from liquid hydrocarbons.

GAS-SOLID REACTIONS PRODUCING A SOLID

$$Ti + N_2 \longrightarrow TiN \qquad (1)$$

$$Mg + N_2 \longrightarrow Mg_3N_2 \qquad (2)$$

$$W + N_2 \longrightarrow WN \qquad (3)$$

$$W + CH_4 \longrightarrow WC + W_2C \qquad (4)$$

$$WO_3 + CH_4 \longrightarrow WC + W_2C \qquad (5)$$

$$Ta + CH_4 \longrightarrow TaC + Ta_2C \qquad (6)$$

$$Ta_2O_5 + CH_4 \longrightarrow TaC + Ta_2C \qquad (7)$$

$$Ta_2O_5 + H_2 \longrightarrow Ta \qquad (8)$$

$$WO_3 + H_2 \longrightarrow W \qquad (9)$$

$$Al_2O_3 + H_2/CH_4 \longrightarrow Al \qquad (10)$$

$$FeO + H_2 \longrightarrow Fe \qquad (11)$$

The production of metal nitrides [8 & 17] from the elements has been investigated for three elements, titanium, magnesium and tungsten (reactions 1 to 3). The production of titanium nitride in the 100% yield was accomplished by using 200 mesh titanium powder fed into a nitrogen plasma jet. The titanium nitride particle size was found to be 0.75 to 7.5 microns and the product was also formed in large, compact, golden yellow crystals. In a like manner tungsten nitride was formed in 25% yield. 40% conversion to magnesium nitride was obtained when magnesium was fed into a nitrogen plasma jet.

The preparation of metal carbides has also been reported [12 & 17]. Figure 5 shows the % conversion vs. Kwhr/g tungsten input for reaction 4. As can be seen, the WC conversion is directly proportional to the power input level. The highest conversions obtained were 43% for W_2C and 11% for WC. Reaction 5 above is shown in Figure 6 where % conversion is plotted vs. Kwhr/g WO_3 input. The three products of the reaction, tungsten (43 to 81% conversion), tungsten carbide (4 to 11% conversion) and ditungsten carbide (9 to 35% conversion) are formed in a total conversion of 81 to 94%. The major product is tungsten which is favored at higher Kwhr/g WO_3 inputs. The reaction of tantalum and methane in a helium plasma jet is shown in Figure 7 where a water-cooled quenching probe was placed at 1/2" and 5" below the plasma jet. The effect of the quenching distance is dramatic. The amount of Ta_2C formed is not appreciably different in either case, however, the TaC yield changed considerably by the placement of the quenching device. Conversions up to 72% TaC have been produced by this reaction. Figure 8 shows a plot of the tantalum-pentoxide plus methane reaction carried out in a helium plasma jet. The % conversion is plotted vs. Kwhr/g tantalum pentoxide input for two different quenching probe distances from the plasma jet. In the case where the quencher was 1/2" below the jet the production of TaC

$W + CH_4$

5 inch quench distance

⊙ △ micron size W

⚲ ⍋ -325 mesh W

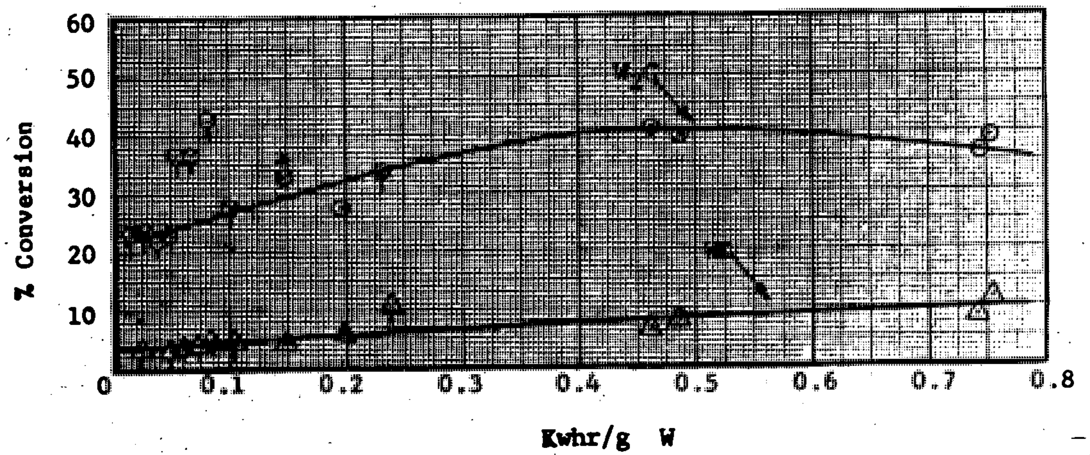
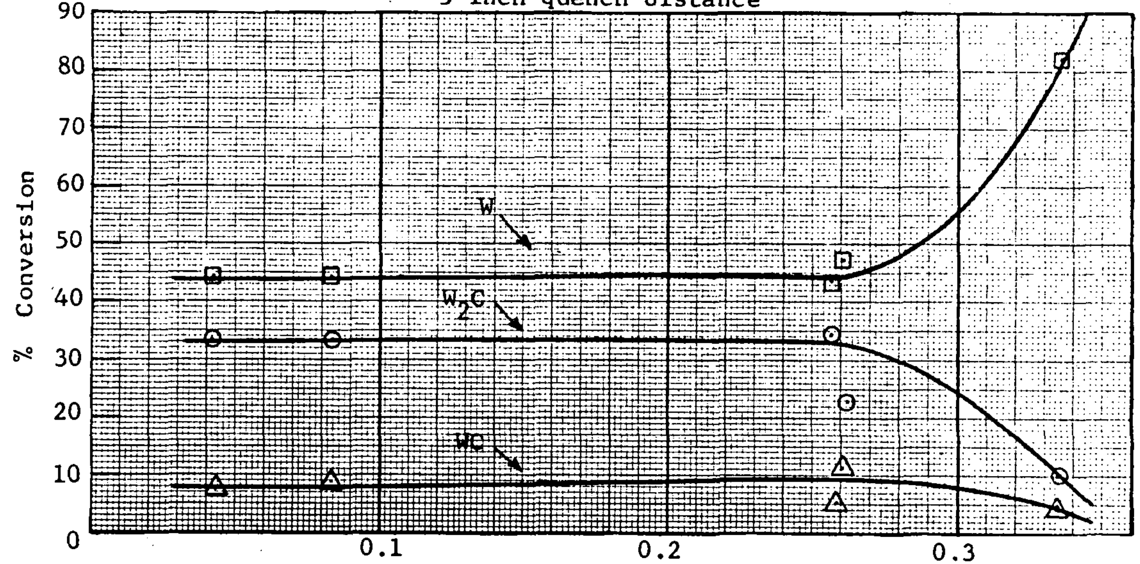


FIGURE 5

$WO_3 + CH_4$

5 inch quench distance



Kwhr/g WO_3

FIGURE 6

Ta + CH_4 IN HELIUM PLASMA JET

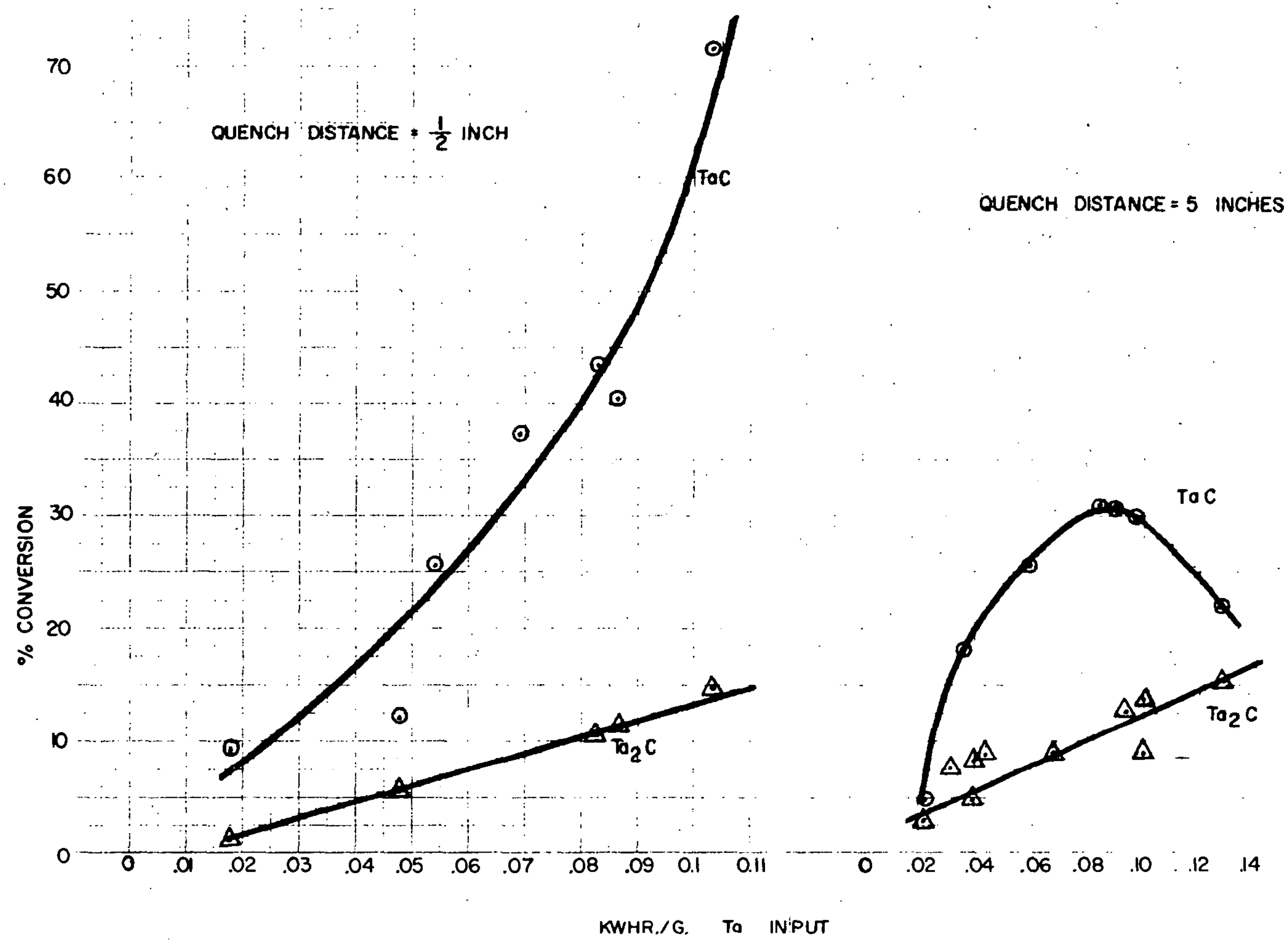
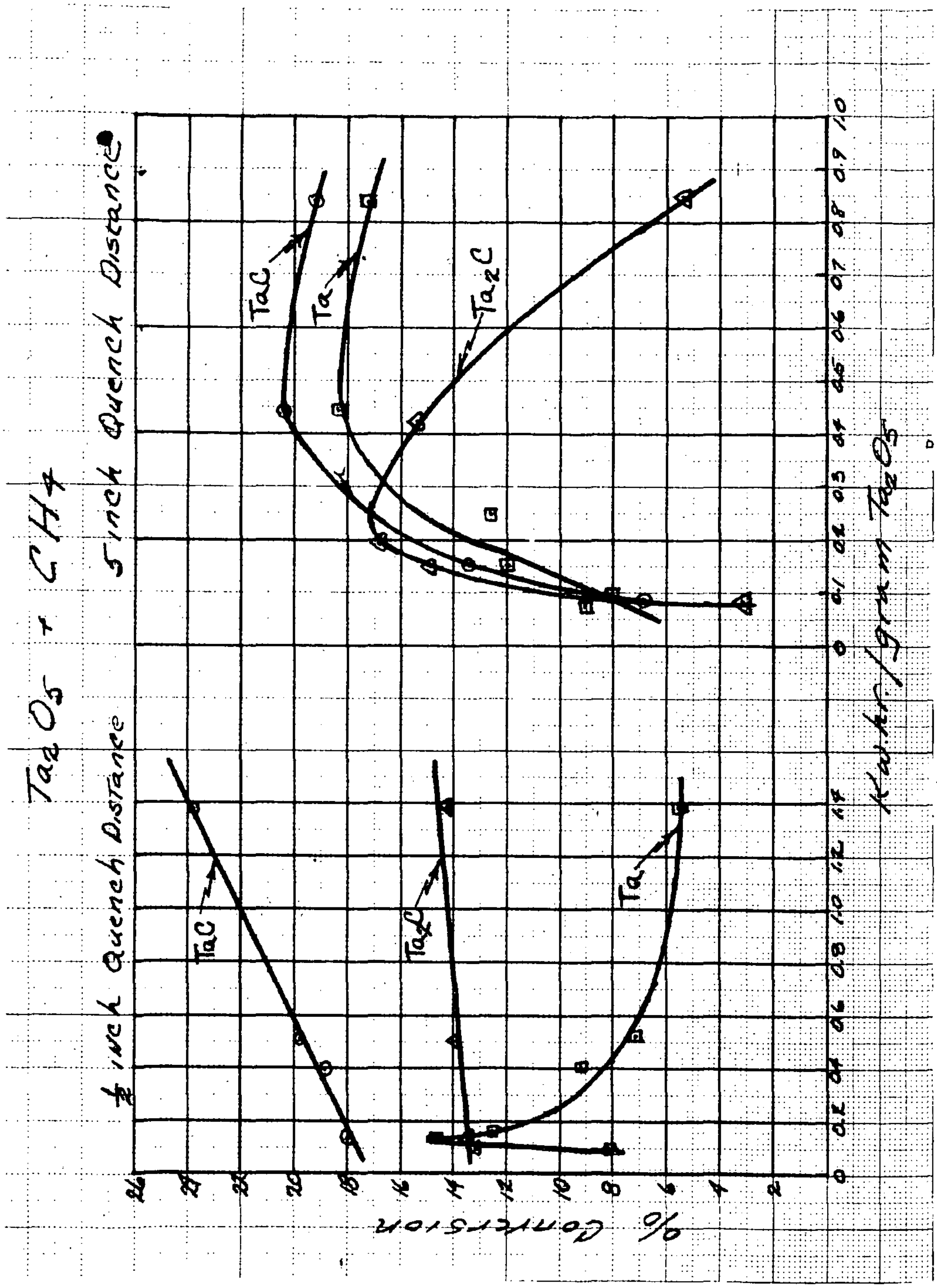


FIGURE 7



Ta2 O5 + CH4
½ inch Quench Distance
5 inch Quench Distance
TaC
Ta
Ta2C
% Conversion
Kw.hr./gram Ta2O5

FIGURE 8

goes up linearally with the Kwhr/g input. Where the quenching distance was 5" a peak was obtained which shows that adequate quenching does not take place beyond a value of 0.4 for Kwhr/g. Note that in the second case the formation of Ta_2C also peaks and then falls off rapidly, in contrast to the 1/2" distance. Tantalum metal is the favored product in the 5" case. Maximum conversions are 24% TaC, 17% Ta_2C and 18% Ta for both cases.

The reduction of tantalum pentoxide with hydrogen (12) in a helium plasma jet to produce tantalum metal (reaction 8) is shown in Figure 9. Again the % conversion is plotted vs. Kwhr/g Ta_2O_5 input for two different quenching distances. As can be seen the more rapid quenching (1/2" case) gives the maximum conversion (42%), which peaks at 0.35 Kwhr/g Ta_2O_5.

In a similar manner the reduction of tungsten trioxide was carried out in a helium plasma jet (17) with the quenching device 5" below the plasma jet. Conversions as high as 95% were obtained carrying the tungsten trioxide in hydrogen into the flame of the jet. The reduction of other metal oxides has also been experimentally investigated (17). Ferric oxide was reduced to iron metal in a 100% conversion using a helium plasma jet and carrying the ferric oxide in hydrogen (reaction 11). Titanium dioxide and zirconium dioxide reductions were also attempted by the same method, however, no reduction was obtained in either case. The reduction of aluminum oxide with hydrogen in a helium plasma jet produced only a 2 to 5% conversion to aluminum metal using several different quenching methods.

LIQUID-GAS REACTIONS PRODUCING A GAS

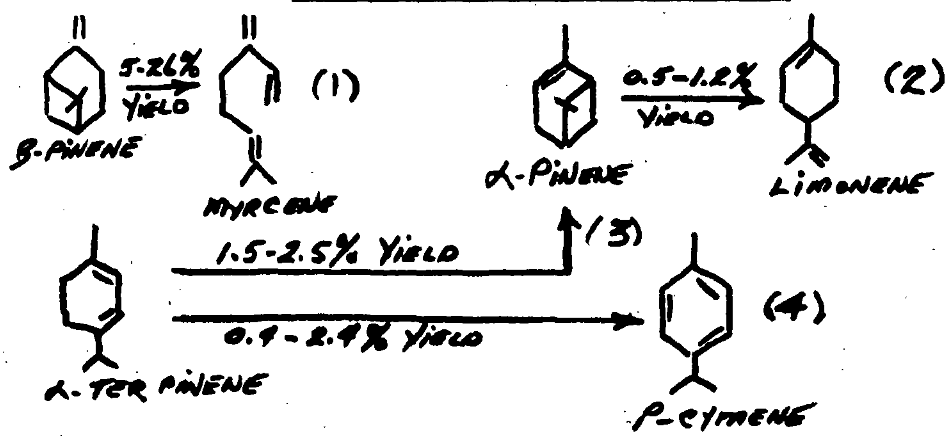
$$\text{Liq. } O_2 \xrightarrow{\text{He plasma}} O_3 \qquad (1)$$

$$\text{Hydrocarbons} \longrightarrow C_2H_2 \qquad (2)$$

The production of ozone by means of a plasma jet was accomplished by feeding liquid oxygen into a helium jet (18). Figure 10 shows the schematic of the apparatus used and Figure 11 shows the effect of liquid oxygen flow on ozone production under constant arc conditions. The liquid oxygen acts as both a reactant and quenching medium.

Another example of this type reactant is the decomposition of hydrocarbons into acetylene by use of a plasma jet device. Thermodynamics Corporation (19) has proved the feasibility of producing acetylene from kerosene using a plasma torch. Preliminary runs gave yields of 18% acetylene.

LIQUID-GAS REACTIONS TO PRODUCE A LIQUID



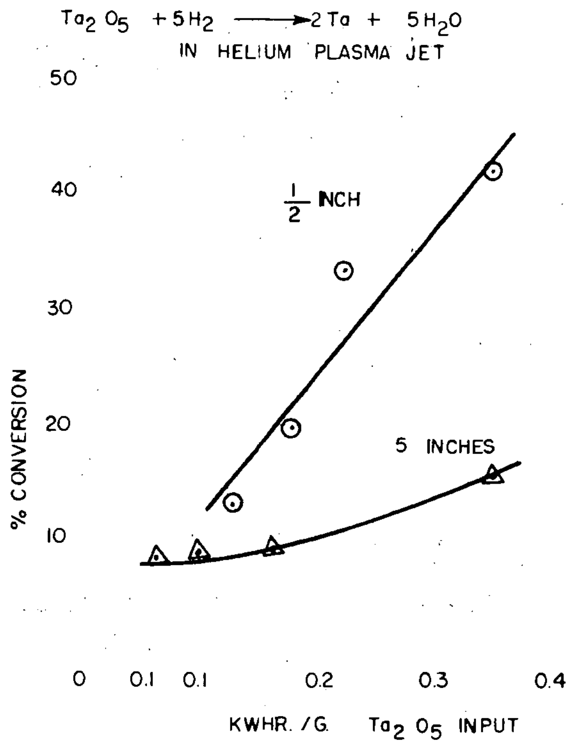

$Ta_2O_5 + 5H_2 \longrightarrow 2Ta + 5H_2O$
IN HELIUM PLASMA JET
50
40
30
20
10
0
0.1
0.1
0.2
0.3
0.4
% CONVERSION
1/2 INCH
5 INCHES
KWHR. /G. Ta_2O_5 INPUT

FIGURE 9

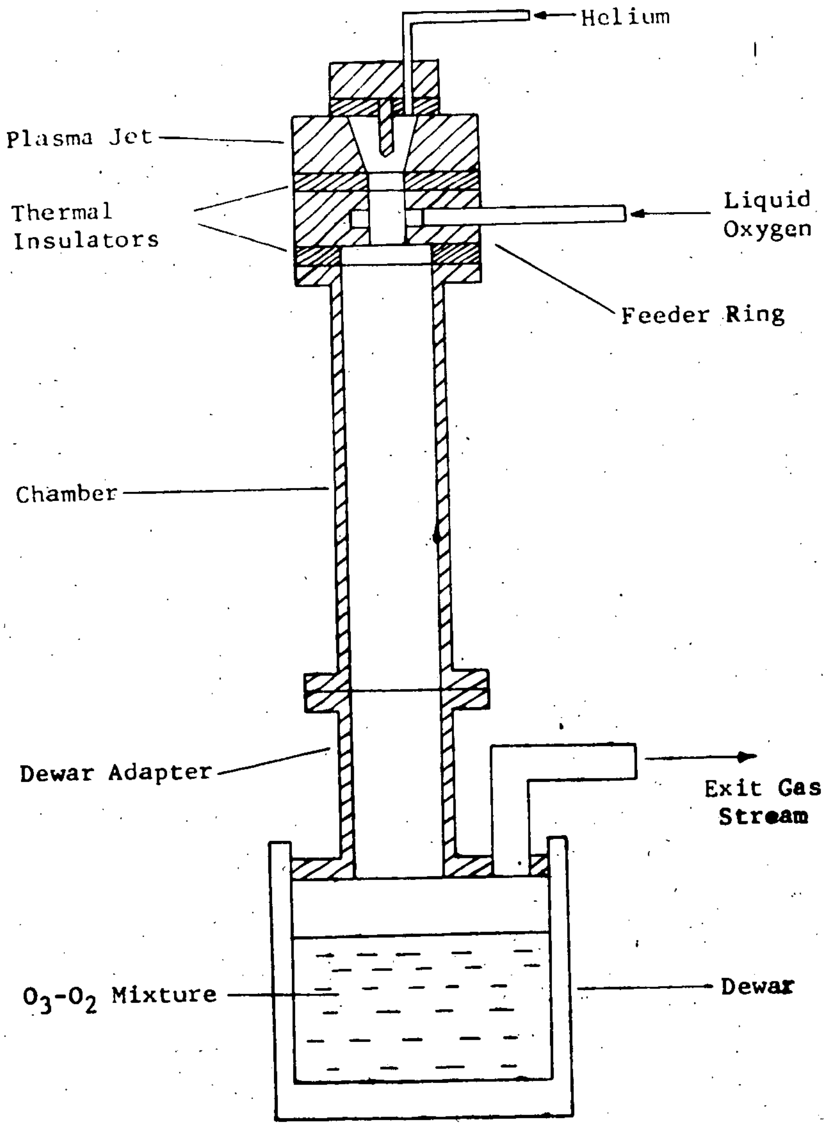
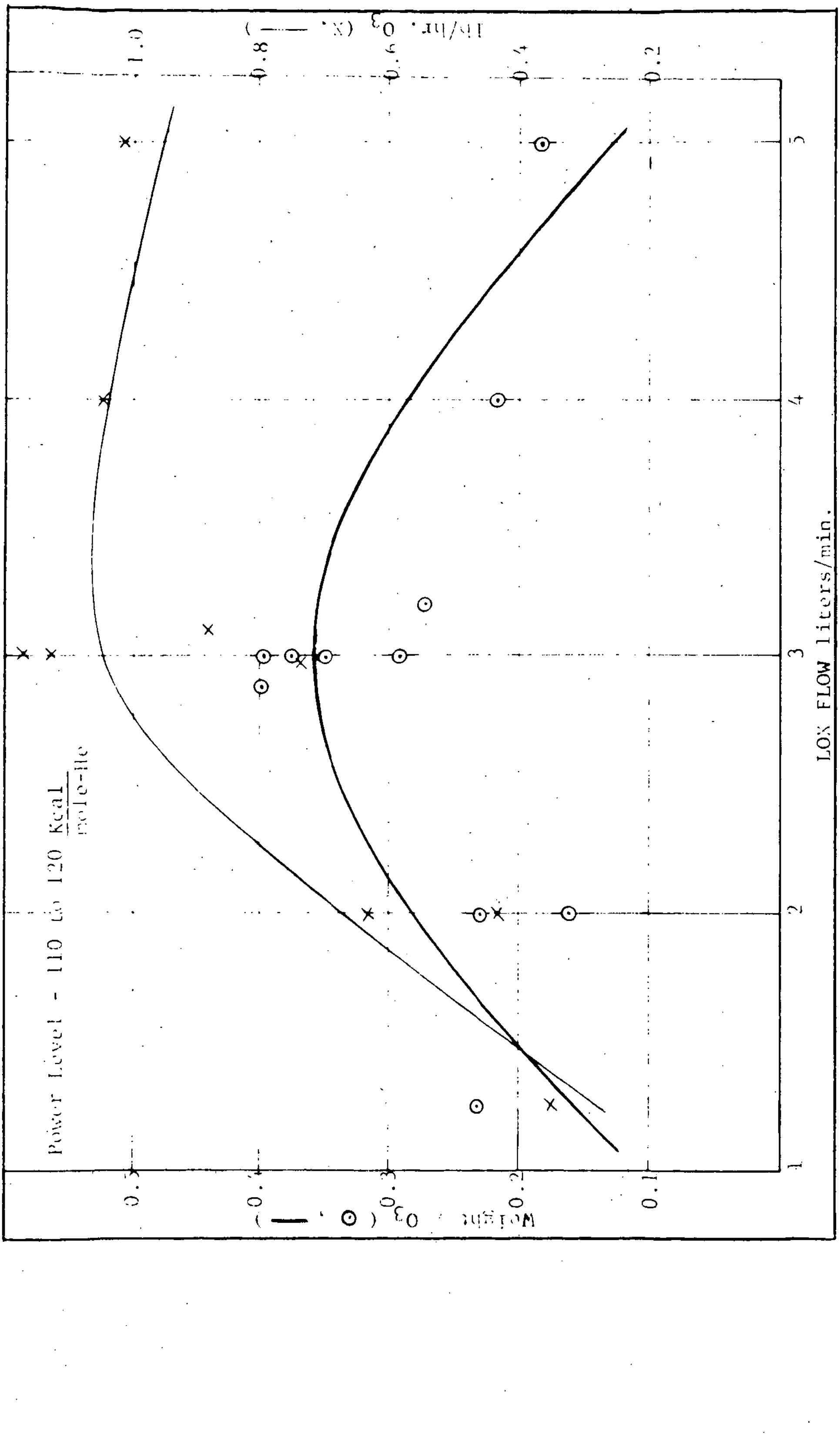

Helium
Plasma Jet
Thermal
Insulators
Liquid
Oxygen
Feeder Ring
Chamber
Dewar Adapter
Exit Gas
Stream
O_3-O_2 Mixture
Dewar

FIGURE 10



Power Level - 110 to 120 Kcal/mole-He
Weight % O3 (⊙, —)
lb/hr. O3 (X, ——)
LOX FLOW liters/min.
0.1
0.2
0.3
0.4
0.5
0.2
0.4
0.6
0.8
1.0
1
2
3
4
5

FIGURE 11

Under program carried on at the Research Institute of Temple University for the Glidden Company the reactions of terpenes in a plasma jet were studied [20]. The reactions shown above were investigated by use of the apparatus showed schematically in Figure 12. All experimental data were obtained using a helium plasma jet where the terpene was added in a liquid state into the helium plasma flame. The products were analyzed by means of chromatigraphic absorption. The most productive synthesis was the conversion of B-pinene to myrcene in 26% yield (reaction 1). Although this is a normal pyrolsis product of B-pinene it is the first time that a complicated molecule has been produced by means of a plasma jet. Other reactions included the preparation of limonene from α-pinene in 1% conversion a nd para-cymene in 2 1/2% yield and α-pinene in 2 1/2% yield from α-terpinene (reactions 2 to 4).

SUMMARY

The chemical reactions discussed above summarize the synthesises that have been accomplished thus far using a plasma jet device and are by no means all the synthesises studied using a plasma jet. The plasma jet has shown itself to be a useful tool in the area of synthesis of compounds and has moved from the preparation of simple materials to more complex ones recently. With the ever increasing number of investigations being carried out by private industry, there is no doubt that the plasma jet will become a commercial chemical process device. Its potential has been just touched and with each new use a whole field of investigation is opened.

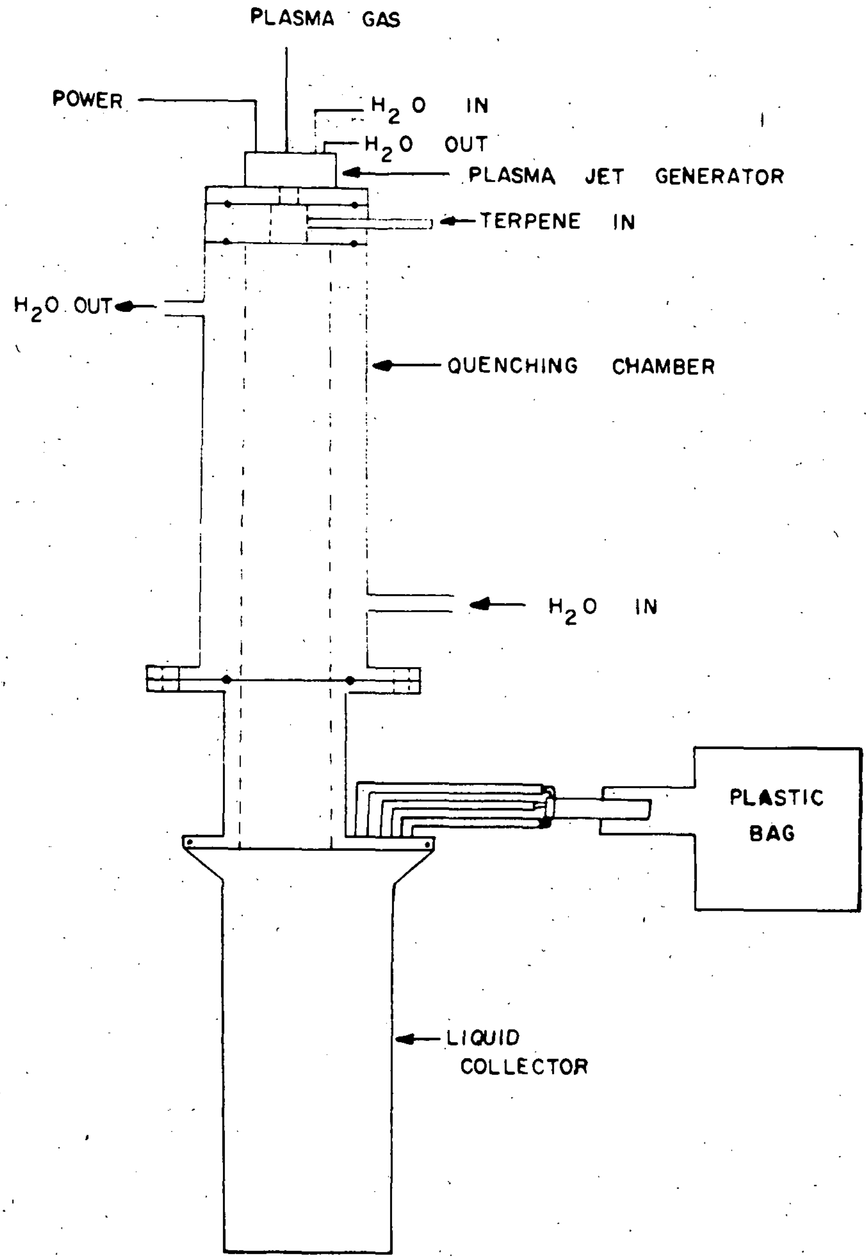

PLASMA GAS
POWER
H2O IN
H2O OUT
PLASMA JET GENERATOR
TERPENE IN
H2O OUT
QUENCHING CHAMBER
H2O IN
PLASTIC BAG
LIQUID COLLECTOR

FIGURE 12

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